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Persistence of Glyphosate Residues in Northern Manitoba Ponds

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Manitoba
Environment and
Workplace Safety
and Health
Environmental
Management Services

PERSISTENCE OF GLYPHOSATE

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SUMMARY

Manfor Ltd. is currently investigating the efficacy of the herbicide Roundup(R) for selective control of competition in conifer plantations. Glyphosate is the active ingredient in Roundup(R) and aminomethylphosphonic acid (AMPA) is its major metabolite. Monitoring of initial Manfor Ltd. field trials in 1985 had suggested that glyphosate and AMPA residues dissipated from surface waters at a rate much faster than had been typically reported in the literature. Because initial results were based on observations of a single water body, there was uncertainty regarding generic applicability of the local observations and, conversely, the applicability of degradation mechanisms reported in the literature. Accordingly, the purpose of the present study was to accurately determine the rate of glyphosate dissipation from water under northern Manitoba conditions. Additionally, the major local mechanism for removal from the water column was to be identified.

A series of six artificial pools was placed in staggered formation at the centre of the 1986 Manfor Ltd. experimental spray block. The spray block was located approximately 63 kilometres north of The Pas in north-western Manitoba. Three pools contained only water and three contained water and sediments. The pools were calibrated for volume and were each sampled seven times within a thirty-day period after herbicide application. Three sampling sites in a nearby natural pond were treated in a similar fashion and provided a comparison to the natural state.

The study confirmed that the presence of sediments was essential for rapid removal of glyphosate from water in northern Manitoba. Glyphosate residues were found to dissipate rapidly from water when sediments were present; 50% of the initial concentration dissipated within approximately 22 hours of application. Maximum AMPA residues encountered in the water were 2.2% of the glyphosate applied. AMPA residues also dissipated rapidly from the water when sediments were present. AMPA dissipation to 1% of applied glyphosate was predicted within approximately 3.9 days of initial herbicide application. Glyphosate residues were comparatively persistent in sediments as evidence of dissipation was not detected during the thirty-day term of the study period.

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1.0 INTRODUCTION

The forest industry in Manitoba has recently begun evaluating the efficacy of Roundup(R) for managing forest vegetation. Typically, the herbicide may be used either to remove vegetation prior to conifer planting or to selectively control competition in conifer plantations (Newton et al., 1984). Glyphosate [N-(phosphonomethyl) glycine] is the active ingredient in Roundup(R).

Manfor Limited proposed initial field trials of glyphosate on conifer plantations near The Pas (53°50', 101°15') during 1984. These initial trials were postponed for one year due to local concern about the herbicide's environmental fate. The trials were subsequently conducted during 1985 and environmental monitoring was instituted (Beck, 1987; Philips, in prep.). Aquatic monitoring indicated that offsite deposition near the spray zone occurred during and immediately following aerial application, but there was no evidence of export off site (op. cit.). Contrary to much of the available literature which cites a half-life in the range of 12 days to 7 weeks (Rueppel et al., 1977; Sacher, 1978; Frazier, unpublished, in Bronstad and Friestad, 1985; Malik, unpublished, in Tooby, 1985), glyphosate residues in local pond waters were reported to dissipate rapidly with an initial half-life of less than 24 hours (Beck, 1987). The rapid rate of dissipation reported by Beck (Ibid) was based on observation of one local pond and was supported by a single reference in the literature (Mestdagh, unpublished, in Tooby, 1985). Thus there was

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Roundup (R) is a registered trademark of Monsanto Company.

some uncertainty regarding generic application of the local observations and, alternately, the applicability to local conditions of degradation mechanisms reported in the literature (Rueppel et al., 1977; Sacher, 1978). Hence, the purpose of the present study was to accurately determine the rate of glyphosate dissipation in water under local conditions. Additionally, the significance of sediments for the removal of glyphosate and AMPA residues from water was to be assessed for local conditions.

2.0 DESCRIPTION OF AREA

The study area (54° 23', 101° 22') is located approximately 580 kilometres northwest of Winnipeg, Manitoba (Figure 1). It lies approximately 63 kilometres north of The Pas and may be accessed from PTH #10 via the Manfor Limited Egg Lake forestry road. The climate is northern continental with less than 100 frost free days per year (Weir, 1983). Mean annual precipitation approximates 425 mm per year, about half of which falls as snow (Ibid). The topography is undulating. Geology of the area is dominated by Ordovician limestones overlain by till (Davies et al., 1962). Soils typically are shallow and range from coarse brunisols on well drained areas to peat deposits on low lying areas (op. cit.). Northern coniferous forest comprises the natural vegetation for the area.

2.1 The Spray Zone

The spray zone was located at NW 33-62-27W. It consisted of a 40 hectare block which had been cut over during 1980-1981 (D. Waugh*, pers. com.). Regrowth of trembling aspen, birch, alder and willow was extensive and ranged up to 4 metres in height. Softwood regrowth was less extensive and appeared limited to jackpine. Residual aspen formed a narrow band across the northern part of the block. A stand of residual black spruce remained in the southwestern quadrant. White spruce had been planted in 1982 (Ibid).

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* D. Waugh, Silvicultural Forester, Woodlands Division, Manfor Limited.

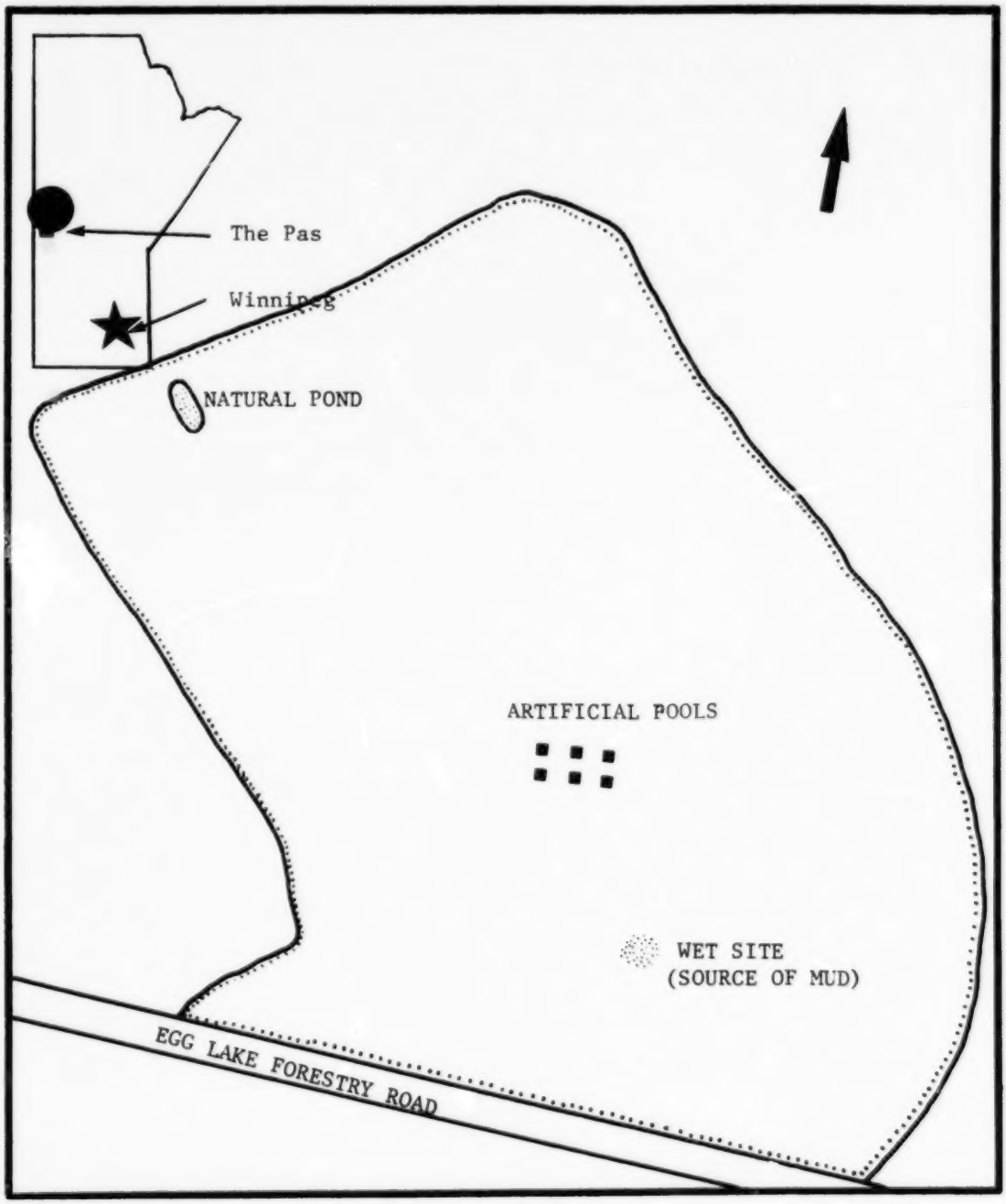

Figure 1: Overview of the study area (40 ha).

One natural pond was located in the northwestern quadrant of the spray zone (Figure 1). The pond consisted of several hundred square metres of dense cattails (Typha sp.) surrounding an open area which measured approximately 3 x 4 metres. Maximum water depth was 25 cm on August 21, 1986, the date of study commencement. The pond was essentially dry by September 4, 1986. Sampling stations A, B and C were located at equidistant intervals along the east-west (long) axis central to the pond.

Artificial pools were located centrally within the spray block (Figure 1). The pools consisted of six injection moulded high density polyethylene tubs measuring 30 x 45 x 30 cm and were calibrated by volume. The tubs were sited in a relatively open area, arranged in a staggered format (Figure 2) and sunk to within 5 cm of ground level. Pools D, E and F contained only water. Pools G, H and I contained a 7 cm (approximate) layer of pond bottom muds in addition to water. The muds had been removed "en masse" from a nearby wet site (Figure 1) and consisted of fine clay material consolidated by a dense root mass. The mud surface was vegetated by mosses, filamentous algae and a variety of herbaceous seedlings.

Herbicide was applied by helicopter commencing at dawn on August 21, 1986. The planned rate of application was approximately 0.89 kg glyphosate per hectare (2.5 L Roundup per hectare; D. Waugh, pers. com.). Wind during application was westerly at 4-8 Kph.

2.2 Water Chemistry

The chemistry of the natural pond water (Table 1) was

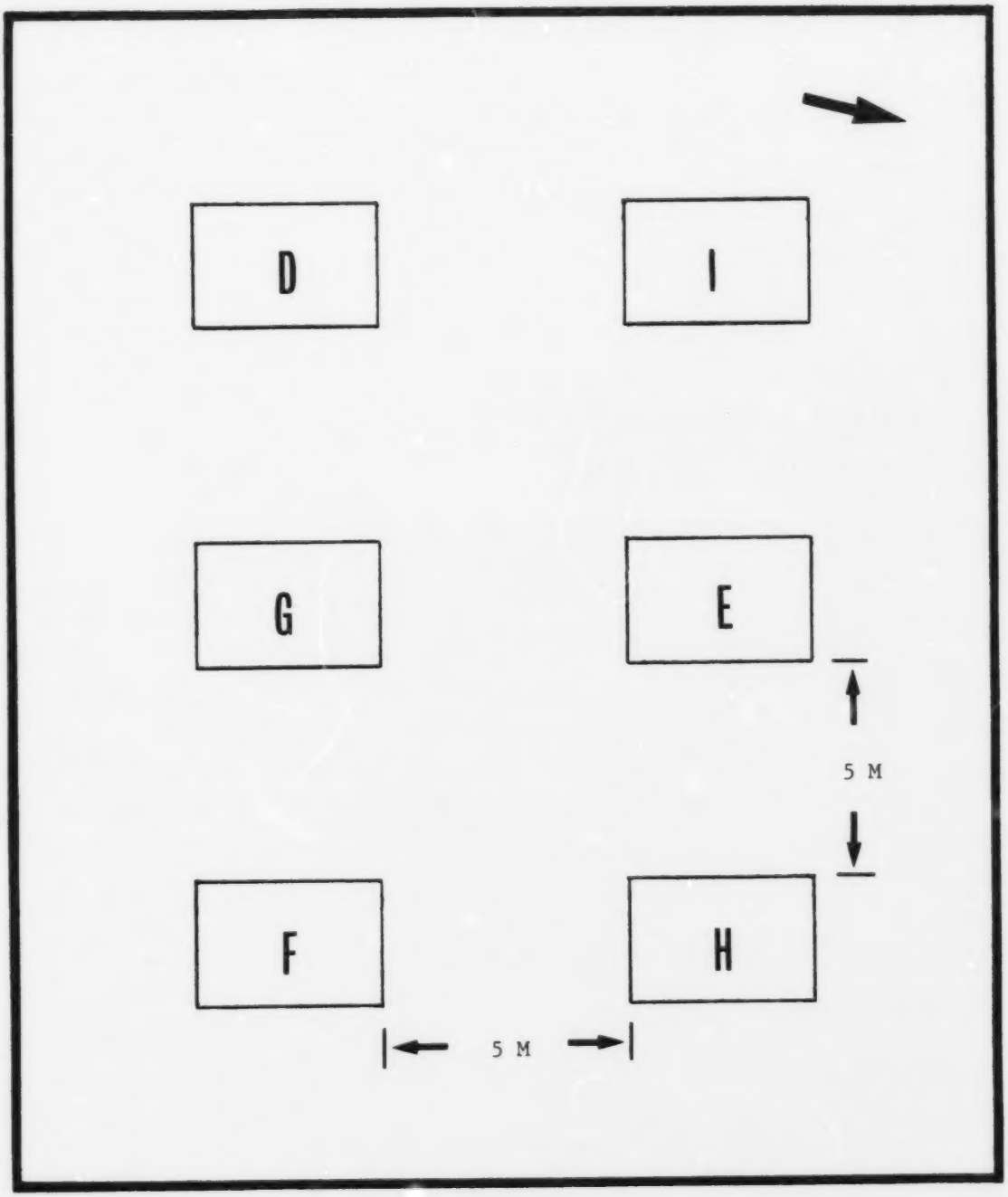

Figure 2: Schematic of artifical pool arrangement.

consistent with its snow meltwater-summer rain source. The water was slightly acidic (pH 6.97; Table 1) and possessed little buffering capacity (total alkalinity 31 mg/L; hardness 43.5 mg/L; Table 1). The conductivity was relatively low (80 uS/cm; Table 1) and the comparatively low levels of dissolved materials present were readily attributable to the effects of di solution from sediments, bioturbation and evaporation.

Water for the artificial pools was obtained from an unnamed stream which originated from Egg Lake. The stream, located approximately 2 kilometres east of the spray zone, was selected as a source because of the shallow depth of nearer water bodies.

The chemistry of artificial pool source waters (artificial ponds, water only, day "0"; Table 1) was considered typical of lakes and streams in the area. Waters were slightly basic (pH 7.88 units; Table 1) and possessed a relatively large degree of buffering capacity (total alkalinity 287 mg/L, hardness 280 mg/L; Table 1). The conductivity was moderately high (513 uS/cm; Table 1) and reflected moderately high levels of dissolved materials. The water chemistry of pools D, E and F changed considerably by the end of the 30 day study period. The increase in pH (7.88 to 8.73 units; Table 1) and the appearance of carbonate alkalinity (0 to 19.93 mg/L; Table 1) were indicative of significant influxes of carbon dioxide and its subsequent dissociation (Hutchinson, 1957). The weak carbonic acid produced by this dissociation in turn may have induced the dissolution of alkalizing materials from the substrate (Kilham, 1982). The inference was that organic matter which had fallen into the ponds

Table 1: WATER MEAN PHYSICOCHEMISTRY*

Parameter		Natural Pond	Artificial Pools (Water Only)		Artificial Pools (Water & Sediments)	
		Day "0"	Day "0"	Day "30"	Day "0"	Day "30"
Conductivity	uS/cm	80	513	483	443	326
pH	Units	6.97	7.88	8.73	7.20	7.37
Total Alkalinity	mg/L	31	287	295	243	186
HCO_3 Alkalinity	mg/L	38	350	319	297	214
CO_3 Alkalinity	mg/L	0.00	0.00	19.93	0.00	0.00
OH Alkalinity	mg/L	0.00	0.00	0.00	0.00	0.00
Calcium	mg/L	9.69	51.10	54.23	47.0	33.83
Magnesium	mg/L	4.71	36.90	41.50	33.75	24.27
Hardness	mg/L	43.50	280	306	257	184
Manganese	mg/L	0.19	0.06	0.02	0.54	0.19
Iron	mg/L	3.32	0.31	0.26	10.32	6.59
Sulphate	mg/L	6.77	12.13	5.20	65.5	8.40
Colour	Units	>50	>50	>50	>50	>50
Turbidity	NTu	2.67	1.25	0.90	1100	22
Potassium	mg/L	5.17	<5.00	<5.00	<5.00	6.83
Total Kjeldhal Nitrogen	mg/L	2.5	1.6	2.5	4.4	5.8
Nitrate-Nitrite Nitrogen	mg/L	<0.01	0.14	<0.01	0.12	<0.01
Total Phosphorus	mg/L	0.20	0.04	0.29	0.23	0.75

* Where: Day "0" is August 18, 1986, three days before spray.
Day "30" is September 19, thirty days after spray.
> is "greater than".
< is "less than".

(leaves, insects, mice, etc.) provided an ideal substrate for intense microbial activity and their subsequent release of carbon dioxide. Depletion of dissolved inorganic nitrogen species (0.14 to <0.01 mg/L; Table 1) and apparent conversion to total Kjeldhal nitrogen (i.e. organic nitrogen, 1.6 to 2.5 mg/L; Table 1) and increases in total phosphorus concentrations (0.04 to 0.29 mg/L; Table 1) provided further evidence of microbial decomposition.

The presence of sediments altered the chemistry of pools G, H and I despite being drawn from the same source as pools D, E and F. Surprisingly, waters initially were less alkaline (pH 7.20 units; Table 1) and possessed less buffering capacity (total alkalinity 243 mg/L, hardness 275 mg/L) than pools without sediments. Iron and sulphate concentrations were substantially greater in the pools with sediments (10.32 vs. 0.31 mg/L, 65.5 vs. 12.13 mg/L; respectively; Table 1). Total Kjeldhal nitrogen and total phosphorus concentrations (4.4 and 0.23 mg/L; respectively; Table 1) were also comparatively high. Most notable was the influence of colloids and fine suspended material added by the sediments; the mean turbidity (1100 units; Table 1) increased approximately 3 orders of magnitude over pools without sediments (1.25 units; Table 1). Chemical changes in pools G, H and I at the end of 30 day term of study closely paralleled those of pools D, E and F. This suggested that a similar microbial fauna were present and operative.

3.0 METHODS

The study was designed to provide triplicate samples for each treatment. Treatments included a natural pond, artificial pools with water only and artificial pools with water and sediments. The term of study was set at 30 days in deference to preliminary indications of an initial half-life of less than 24 hours (Beck, 1987).

3.1 Field Procedures

Sampling frequency for glyphosate was set at before application, within 30 minutes after application, 30 hours after application and at post application intervals of 5, 8, 15, 20 and 30 days thereafter. Water physicochemistry samples were collected before application and at the 30-day interval.

Artificial pool water volumes were recorded prior to all sampling. Polyethylene whirlpacs were worn as gloves and discarded after each pool was sampled in order to prevent cross contamination. Complete mixing of artificial pool waters was assured by hand stirring for approximately 1 minute prior to collection of the first post-application samples.

Glyphosate water samples were collected by immersing new 1 L polyethylene bottles that had been triple rinsed with several millilitres of site water. Approximately 100 g of sediments from sites A, B and C of the natural pond and from artificial pools G, H and I were collected by hand grab and placed in whirlpacs. A single

template of pool wall* was also collected during each sampling interval and placed in a whirlpac. Samples destined for glyphosate analysis were stored on ice not longer than 3 hours during transit prior to placement in freezers. Upon completion of all field activities, frozen samples were packed with dry ice and couriered by air to A & S Environmental Testing, Inc.** for analysis.

Samples for physicochemical analysis were also collected by immersion of triple rinsed bottles. Unlike the glyphosate samples, physicochemical samples were iced and shipped by scheduled bus service so as to arrive at the analytical facility*** within 24 hours of collection.

3.2 Analytical Procedures

The procedure used for herbicide analysis of water and sediments was an unpublished confidential method entitled "HPLC-Fluorometric Method for the Analysis of Glyphosate and

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* Templates, consisting of precut 10 x 10 cm sections of tub wall, were suspended in pool G during installation of artificial pools. The intent was to test for glyphosate adsorption to the pools walls.

** Address: P.O. Box 130, Temple, Pennsylvania, USA. 19560

*** W. M. Ward Technical Services Laboratory,
745 Logan Avenue, Winnipeg, Manitoba. R3E 3L5

Aminomethylphosphonic Acid in Raw Agricultural Commodities and Water" (S. Stupp*, pers., com.). The instrument used was a Kratos Spectroflow 980 Fluorescence Detector with the PCRS 520 dual-heated post column reaction system (Ibid). Columns were a 3.0 mm x 25 cm Ion-110 with Alltech C_{18} precolumn and then an Ion Guard GA-100 guard column (Ibid). The mobil phase used was 0.005 m potassium dihydrogen phosphate in 4% methanol/deionized water at pH 2.10 (Ibid).

Templates were extracted overnight with 10% HCl (S. Stupp, pers. com.). The extract was then analyzed as a water sample (Ibid).

Physicochemical analysis of water samples was conducted according to procedures described by Sorba et al. (1980).

3.3 Assessment of Analytical Accuracy

Analytical accuracy for glyphosate in water was tested by blind submission of a series of eight spiked (1.2 to 159 µg glyphosate/L) samples. Spikes were prepared from commercial Roundup^{R} formulation by dilution with water drawn from the same source as that of the artificial ponds. Spikes were frozen immediately after preparation (L. Prokopanko**, pers. com.) and were submitted blind for analysis along with regular samples.

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* S. Stupp; Director of Pesticide Chemistries, A & S. Environmental Testing, Inc.

** L. Prokopanko; Chemist, Quality Assurance, W. H. Ward Technical Services Laboratory.

Analytical accuracy for residues in water of aminomethylphosphonic acid (AMPA), the major metabolite of glyphosate (Rueppel et al., 1977), was not tested because stock reagent could not be obtained (L. Prokopanko, pers. com.).

Analytical accuracy for glyphosate and AMPA residues in sediments were not tested.

Detection limits for both glyphosate and AMPA were tested by submission of a series of nine blank samples. (A single sample was drawn from each sampling site prior to herbicide application. These were treated with various concentrations of glyphosate and submitted as regular samples.) The upper 95% confidence interval was calculated from blank data and considered the minimum limit of detection.

4.0 RESULTS AND DISCUSSION

4.1 Analytical Accuracy

Quality control data (Table 2) was evaluated in order to develop appropriate corrective factors. These efforts were limited to the aqueous phase and, subsequently, comments apply only to residues in water.

4.1.1 Minimum Detection Limits

Minimum detection limits were calculated in order to quantify background interference (false low level detections) and to reduce the probability (P = 0.05) of reporting a false detection. Low level interference has been reported for AMPA using the HPLC analytical technique (Bardalaye et al., 1985) and was encountered in both glyphosate and AMPA analysis during the initial (1985) Manfor Ltd. field trials (Beck, 1987). The minimum detection limit for glyphosate residues computed for the present study was 1.7 µg/L (Table 2). This was approximately three times greater than the capability (0.50 µg/L) reported by the analytical facility (S. Stupp, pers. com.). However, this represented an improvement over the 2.2 µg/L limit derived for the initial trials (Beck, 1987). The minimum detection limit for AMPA residue computed for the present study was 0.5 µg/L (Table 1). This matched the capability reported by the analytical facility (S. Stupp, pers. com.) and was greatly improved compared to the 9.05 µg/L limit (Beck, 1987) derived during initial Manfor Ltd. trials.

Table 2: QUALITY CONTROL DATA FOR WATER SAMPLES

PART A: PRESPRAY BLANK SAMPLES

Sample	Reported Glyphosate (µg/L)	Reported AMPA (µg/L)
A	<0.50	<0.50
B	<0.50	<0.50
C	<0.50	<0.50
D	<0.50	<0.50
E	0.75	<0.50
F	4.0	<0.50
G	<0.50	<0.50
H	<0.50	<0.50
I	<0.50	<0.50
Mean ± standard deviation	0.92 ± 1.16	<0.50 ± 0
Upper 95% Confidence Limit	1.7	0.50

PART B: GLYPHOSATE SPIKED SAMPLES

Sample	True Glyphosate (µg/L)	Reported Glyphosate (µg/L	% Recovery
1	1.2	1.4	117%
2	6.3	4.9	78%
3	12.7	5.8	46%
4	12.4	6.6	53%
5	31.4	19	61%
6	62	61	98%
7	65	56	86%
8	159	85	53%
Mean	-	-	74%

4.1.2 Analytical Recovery Rate

Reported glyphosate recovery rates for HPLC analysis of various agricultural product extracts ranged from 70%-107% (Bardalaye et al, 1985). The mean glyphosate recovery rate during initial Manfor Ltd. field trials was 115% (Beck, 1987). The analytical facility reported a mean rate of glyphosate recovery from water of 100% (S. Stupp, pers. com.) during the present study. Recoveries from spiked samples submitted blind ranged from 46% to 117%, with a mean of 74% (Table 2). Consequently, analytical results for glyphosate residues in water were corrected by a factor of 1.35 and were so reported.

The mean rate of AMPA recovery from water during the present study was reportedly 97% (S. Stupp, pers. com.). Though this could not be independently substantiated, it compared reasonably well with the mean 85% rate reported during initial trials (Beck, 1987). Hence, further correction for analytical losses was not required and results for AMPA were reported as received from the analytical facility.

The mean glyphosate sediment recovery rate was 61% (S. Stupp, pers. com.). Results were reported as received because independent substantiation was not available.

4.1.3 Pool Wall Adsorption

The insolubility of glyphosate in organic solvents (Franz, 1985) suggested that the herbicide would neither absorb nor appreciably adsorb to the high density polyethylene walls of the artificial pools. This assumption was supported by experimental data

Table 3: APPARENT GLYPHOSATE AND AMPA RESIDUES (µg) EXTRACTED FROM 10 cm x 10 cm SECTIONS OF ARTIFICIAL POOL WALL.

Post Spray Sampling Interval	Glyphosate (µg)*	AMPA (µg)**
Before Spray	1.3	<0.05
30 minutes	5.3	1.95
36 hours	3.7	0.81
5 days	2.6	0.47
8 days	0.7	0.39
15 days	6.2	4.02
20 days	41	8.85
30 days	1.9	0.50

* Glyphosate residues corrected for mean recovery rate of 74%.

** AMPA residues as reported by analytical facility.

(Table 3). Glyphosate and AMPA residues apparently extracted from sections of the pool wall (Table 3) were not significantly correlated with duration of the study (r = 0.32 for both glyphosate and AMPA). Also, apparent residues were not significantly correlated to residues present in water (glyphosate r = 0.36, AMPA r = 0.30). However, a significant correlation (r = 0.95) was observed for a regression of AMPA residues to glyphosate residues. The inference was that apparent residues were derived from varying amounts of sediments and/or water "beaded" on the surface of pool wall sections rather than extracted from the wall section themselves. Therefore, correction for losses to the pool walls was not required.

4.2 Residues in Water

Glyphosate and AMPA residues in water are presented in Table 4. Data from artificial pools were not corrected for changes in volume (Table 5) nor were standard volumes maintained (Friestad, 1978; Bronstad and Friestad, 1985). These actions were not taken in order that kinetics in the artificial pools might more accurately reflect the natural state (conditions at sites A, B. and C).

4.2.1 Artificial Pools with Water Only

The planned rate of glyphosate application was 0.89 Kg/hectare, which corresponded to 89 mg/m^2. The estimated instantaneous post-spray glyphosate concentration (C_{GE}) was computed

Table 4: GLYPHOSATE AND AMPA RESIDUES IN WATER

Post-spray Sampling Interval	NATURAL POND GLYPHOSATE (µg/L)* Site A	Site B	Site C	AMPA (µg/L)** Site A	Site B	Site C
30 minutes	43	51	55	0.46	0.77	0.57
30 hours	3.4	<1.7	4.2	<0.5	<0.5	<0.5
5 days	<1.7	3.4	2.4	<0.5	<0.5	<0.5
8 days	<1.7	<1.7	2.8	<0.5	<0.5	<0.5
15 days	dry	dry	dry	dry	dry	dry
20 days	dry	dry	dry	dry	dry	dry
30 days	dry	dry	dry	dry	dry	dry

Post-spray Sampling Interval	ARTIFICIAL POOLS, WATER ONLY GLYPHOSATE (µg/L)* Pool D	Pool E	Pool F	AMPA (µg/L)** Pool D	Pool E	Pool F
30 minutes	326	376	353	1.7	1.9	2.1
30 hours	328	768	722	4.1	6.2	5.2
5 days	651	789	897	7.6	7.8	8.0
8 days	649	724	862	7.4	10	14
15 days	976	747	641	7.7	13	19
20 days	968	305	473	10	7.4	14
30 days	876	305	607	11	12	18

Post-spray Sampling Interval	ARTIFICIAL POOLS, WATER & SEDIMENTS GLYPHOSATE (µg/L)* Pool G	Pool H	Pool I	AMPA (µg/L)** Pool G	Pool H	Pool I
30 minutes	293	331	20	2.2	2.9	0.62
30 hours	284	182	61	12	8.9	3.0
5 days	170	104	32	11	12	2.5
8 days	37	31	15	2.9	5.4	1.3
15 days	19	23	15	0.93	2.2	1.0
20 days	19	5.8	4.9	1.5	0.82	0.93
30 days	15	12	3.1	1.2	1.5	0.62

* Glyphosate residues corrected for mean recovery rate of 74%.

** AMPA residues as reported by analytical facility.

by [$C_{GE} = Ap \cdot R \cdot V^{-1}$]*. The mean C_{GE} for artificial pools containing only water was thus calculated at 302 µg/L. This corresponded reasonably well to the mean glyphosate concentration observed (C_{GO}) in pools D, E and F (352 µg/L; Table 4) within thirty minutes following application.

Glyphosate concentrations in waters located within the spray zones typically peak immediately after aerial application then gradually dissipate (Rueppel et al., 1977; Sacher, 1978; Newton et al, 1984). Hence maximum glyphosate concentrations (C_{GM}) were anticipated for samples collected within 30 minutes of application. However, the C_{GM} were encountered more than 30 hours after aerial application (Figure 3). Apparent relative stability of C_{GO} after the 5-day post-application sampling interval suggested that the actual C_{Gm} developed between the 30-hour and 5-day sampling intervals (Figure 3). This was strongly indicative of additional glyphosate loadings by a vector(s) other than the initial aerial application.

One such vector may have been the hair of small mammals which drowned in the artificial pools shortly after (i.e. less than five days) herbicide application. Although only two of the artificial pools containing solely water held small mammals at the 30-hour

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*Where: Ap = pool surface area = 0.3 m x 0.45 m = 0.135 m^2;
R = rate of application = 89 mg/m^2;
V = volume of pool at the 30-minute post-spray interval, per Table 5.

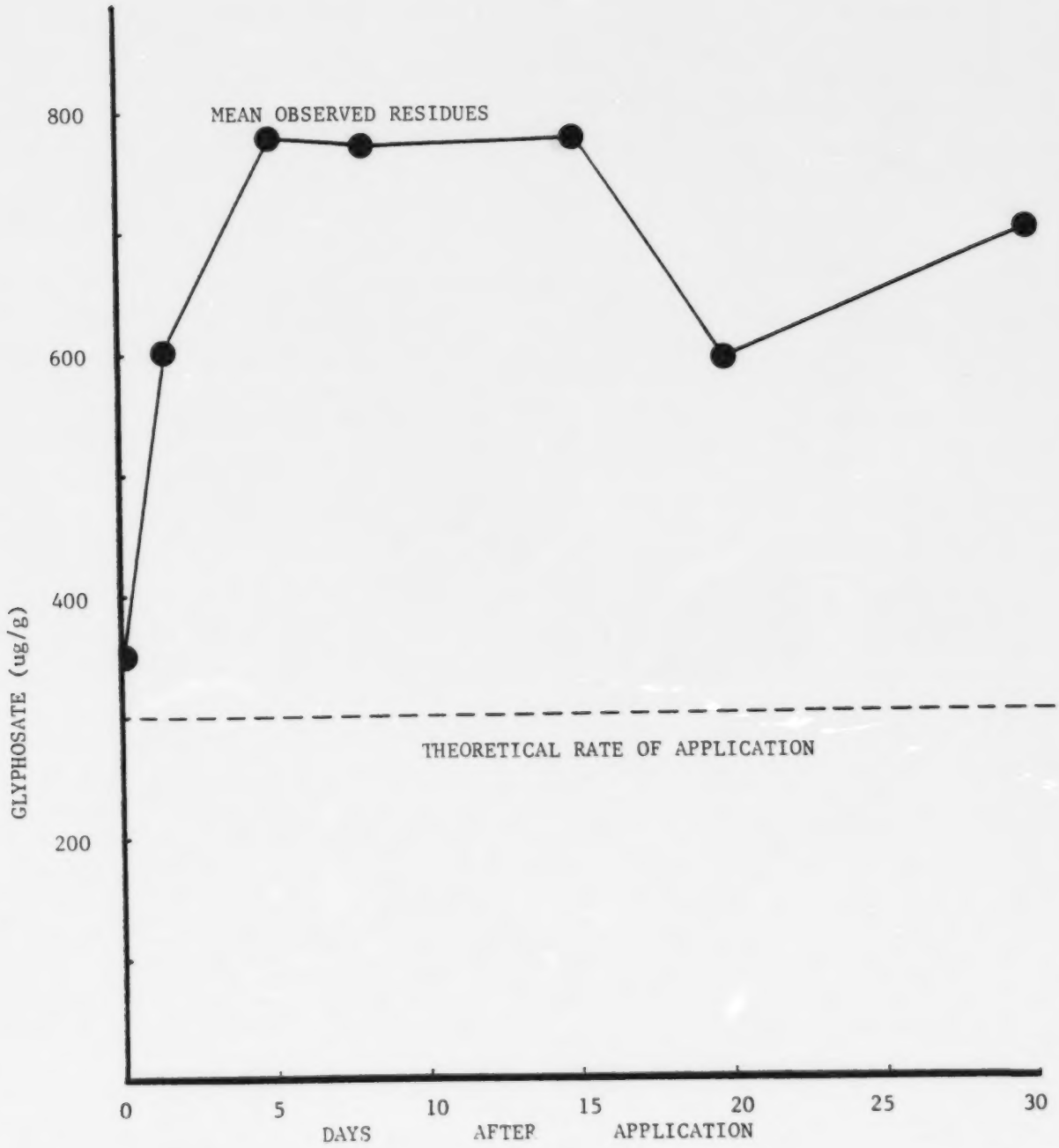

Figure 3: Mean Glyphosate Residues (ug/g) over time in artificial pools containing only water.

Table 5: WATER VOLUME (L) OF ARTIFICIAL POOLS

Post-spray Sampling Interval	Pool D	Pool E	Pool F
Before spray	40	41	41.5
30 minutes	39	40	40.5
30 hours	37	39	37
5 days	35	38	35
8 days	33	35	33
15 days	32	33	31
20 days	31	32	30
30 days	30	30	27

Post-spray Sampling Interval	Pool G	Pool H	Pool I
Before spray	40.5	40.5	33
30 minutes	39.5	39.5	32
30 hours	37	36.5	30
5 days	35	35	29
8 days	31	32	26
15 days	29	30	25
20 days	26	26	23
30 days	25	24	21

sampling interval, all artificial pools held a variety* of drowned small mammals at subsequent sampling intervals. It was hypothesized that the hair of small mammals acquired a coating of glyphosate during passage through sprayed vegetation and during the aerial application; upon drowning in the confined limits of the artificial pool, the coating dissolved and constituted a significant source of glyphosate loading. This hypothesis fitted the empirical evidence. However, the literature provided no corroboration since examination of small mammal responses to glyphosate application were limited to demographics (Sullivan and Sullivan, 1981) and visceral uptake versus body burden (Newton et al., 1984).

Regardless of vector, the data (Table 4, Figure 3) left no doubt that additional loading had occurred. This had implication for evaluation of AMPA data because, as a metabolite (Rueppel et al., 1977; Sacher, 1978), AMPA residues at time T_i may intuitively be presumed to be proportional to glyphosate concentrations at time T_i. Accordingly, evaluation of AMPA results required empirical standardization on the basis of apparent quantitative loading. Standardization was provided by $A_c = A_i \cdot (G_i \cdot G_A^{-1})$** and the rate of

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* Mammals included the deer mouse Peromyscus maniculatus (predominent), the red-back vole Clethrionomys gapperi, the common shrew Sorex cinereus and the pygmy shrew Microsorex hoyi.

** Where:

A_C = standardized AMPA concentration at time "i"
A_i = observed AMPA concentration at time "i"
G_i = observed glyphosate concentration at time "i"
G_A = observed glyphosate concentration at the 30 minute sampling interval.

Table 6: RATE OF AMPA GENERATION (% OF GLYPHOSATE APPLIED) VERSUS TIME (DAYS) IN ARTIFICIAL POOLS CONTAINING ONLY WATER.

Sampling Interval	AMPA (% OF GLYPHOSATE APPLIED)			
	Pool D	Pool E	Pool F	Mean
30 hours	0.13	3.37	3.01	2.17
5 days	4.56	4.35	5.76	4.89
8 days	4.52	5.12	9.68	6.44
15 days	7.07	6.87	9.77	7.90
20 days	9.11	1.60	5.31	5.34
30 days	9.07	2.59	8.77	6.81

AMPA generation was then calculated as a percent of initial observed glyphosate concentration (Table 6). The rate of AMPA generation was curvilinearly correlated ($r = 0.54$) to the length of time after herbicide application (Figure 4).

Three pathways of glyphosate dissipation in waters are possible; microbial, photolytic and adsorption to sediment (Bronstad and Friestad, 1985). Chemical degradation is not considered operative to any significant degree (Rueppel et al., 1977). The short term (i.e. 30-day) natural logarithmic rate of AMPA generation observed (Figure 4) provided no ready means of distinction between photolysis and microbial degradation. However, it was apparent that glyphosate was subject to minor degradation in the absence of sediments and that these mechanisms were either inoperative or operative to a lesser degree upon AMPA (Figure 4). Were this not the case, standardization procedures would have yielded a zero slope for the regression.

4.2.2 Artificial Pools with Water and Sediments

The artificial pools containing water and sediments (pools G, H and I) were located in staggered formation (Figure 2) with the artificial pools which contained only water (pools D, E and F). Thus each of the artificial pools were presumed to be subject to similar planned rates of glyphosate application (89 mg/m^2). The C_{GE} for pools G, H and I were calculated at 304, 304 and 373 µg/L, respectively. The C_{GE} corresponded exceptionally well with the C_{GO} in pools G and H at the thirty minute sampling interval (293 and 331 µg/L, respectively; Table 4), but did not correspond with C_{GO}

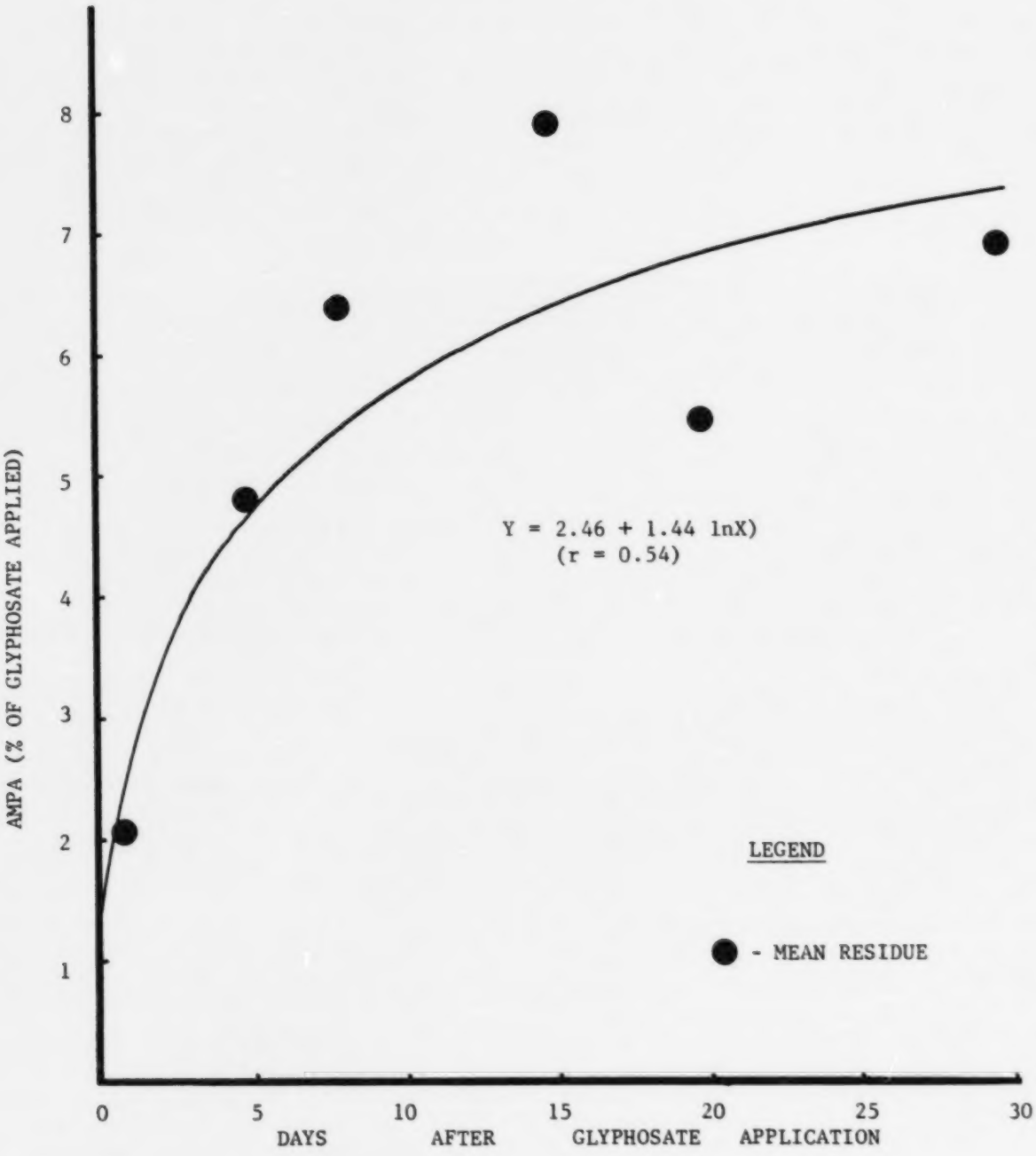

Figure 4: Rate of AMPA generation (% of glyphosate applied) in artificial pools containing only water.

in pool I (20 µg/L; Table 4). This suggested that artificial pool I had been shielded by adjacent alder shrubs and had not received a full dosage of glyphosate during aerial application.*

The staggered formation (Figure 2) and the presence of drowned small mammals in both sets of pools led to the assumption that the additional loading observed in pools D, E and F also occurred at a similar rate on pools G, H and I. Quantitative loading estimates for pools G, H and I were derived from the mean additional loading rate observed per pool (R_A)** for pools D, E and F during the 30-hour and 5-day sampling intervals, (9,672 and 15,372 µg/pool respectively). Estimates of potential maximum concentrations for each of pools G, H and I were then calculated (Table 7). These estimates permitted subsequent calculation of percent glyphosate remaining in pools G, H and I at various sampling intervals (Table 8).

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* Reanalysis subsequently confirmed initial results.

** Computed by $R_{AT} = V_{PT} \cdot (G_{PT} - G_{PO})$;
Where:
R_{AT} = additional loading at time "T"
V_{PT} = volume in pool "P" at time "T"
G_{PT} = glyphosate concentration in pool "P" water at time "T"
G_{PO} = glyphosate concentration in pool "P" water 30 minutes after application
T = Time "T" may alternately be 30 hours or 5 days.

It was assumed that photolytic degradation of glyphosate during the short term was negligible since AMPA residues approximated 1% of total glyphosate applied to pools D, E and F (Table 4).

Table 7: ESTIMATED POTENTIAL MAXIMUM CONCENTRATIONS OF GLYPHOSATE IN WATER OF POOLS G, H AND I DURING 30 HOUR AND 5 DAY SAMPLING INTERVALS, ASSUMING ZERO DISSIPATION

Post-application Sampling Interval	Estimated Maximum Concentration* (µg/L)		
	Pool G	Pool H	Pool I
30 hours	554	596	342
5 days	732	770	550

* Estimated by $G_E = (R_A \cdot V_P^{-1}) + G_{PI}$

where:

G_E = estimated potential maximum glyphosate concentrations

R_A = mean additional loading rate, computed at 9672 µg for 30-hour sampling interval and 15370 µg for 5-day sampling interval;

V_P = Volume in pool "P" at the respective 30 hour or 5-day sampling interval;

G_{PI} = observed glyphosate in pool "P" waters at the 30-minute sampling interval.

Table 8: ESTIMATED GLYPHOSATE RESIDUES (% OF APPLIED) AT VARIOUS TIME INTERVALS IN POOLS G, H and I.

Sampling Interval	Estimated Glyphosate Residues (%)			
	Pool G	Pool H	Pool I	Mean
30 hour *	51.3	30.5	17.8	33.2
5 day **	23.2	13.5	5.8	14.2
8 day **	5.1	4.0	2.7	3.9
15 day **	2.6	3.0	2.7	2.8
20 day **	2.6	0.8	0.9	1.4
30 day **	2.0	1.6	0.6	1.4

* Calculated by: $D_{P30} = 100 \cdot (G_{P30} \cdot G_{EP30}^{-1})$;
where D_{P30} = Glyphosate residues (%) in pool "P" water at 30 hours after application;
G_{P30} = Glyphosate concentration in pool "P" water at 30 hours after application (Table 4);
G_{EP30} = Estimated potential maximum glyphosate concentration in pool "P" water at 30 hours assuming zero dissipation (Table 7).

** Calculated by: $D_{P>30} = 100 \cdot (G_{P>30} \cdot G_{EP>30}^{-1})$;
where $D_{P>30}$ = Glyphosate residues (%) in pool "P" water more than 30 hours after application;
$G_{P>30}$ = Glyphosate concentration observed in pool "P" water more than 30 hours after application (Table 4);
$G_{EP>30}$ = Estimated potential maximum glyphosate concentration in pool "P" water more than 30 hours after application assuming zero dissipation (Table 7).

A regression was developed from estimated glyphosate residues at various time intervals (Table 8) in order to define the rate of dissipation (Sacher, 1978). Unlike Sacher (Ibid), present data (Figure 5) indicated that glyphosate dissipation appeared to follow second order kinetics and could be expressed in the equation $G_X = 45.01\ X^{-1.09}$, ($r = 0.91$), where "G_X" is the glyphosate concentration (%) at time "X" (days). This expression estimated that 50% of the glyphosate dissipated approximately 22 hours after application (Figure 5). It further estimated that 25% of the glyphosate would be present approximately 41 hours after application, 10% would be present approximately 4 days after application and that approximately 1% would be present 30 days after application. This compared favourably to the half-life ($t_{1/2}$) of 12 hours obtained by Mestdagh (unpublished, in Tooby, 1985) and the $t_{1/2}$ of <24 hours obtained during initial Manfor Ltd. field trials (Beck, 1987). Thus it was concluded that glyphosate dissipates rapidly from water ($t_{1/2}$ = 22 hours) when it enters water bodies in northern Manitoba.

The relative persistence of glyphosate in pools containing only water (Figure 3) as compared to pools containing water and sediments (Figure 5) confirmed that the presence of sediments was essential for rapid dissipation of glyphosate from the water. This was consistent with the literature (Comes et al., 1976; Hance, 1976; Edwards et al., 1980; Hurle and Walker, 1980).

Metabolites and other degradation products of pesticides may be more toxic than the parent compound (Butler, 1968) or they may persist for a greater period of time (Bulkley et al., 1981). Thus it

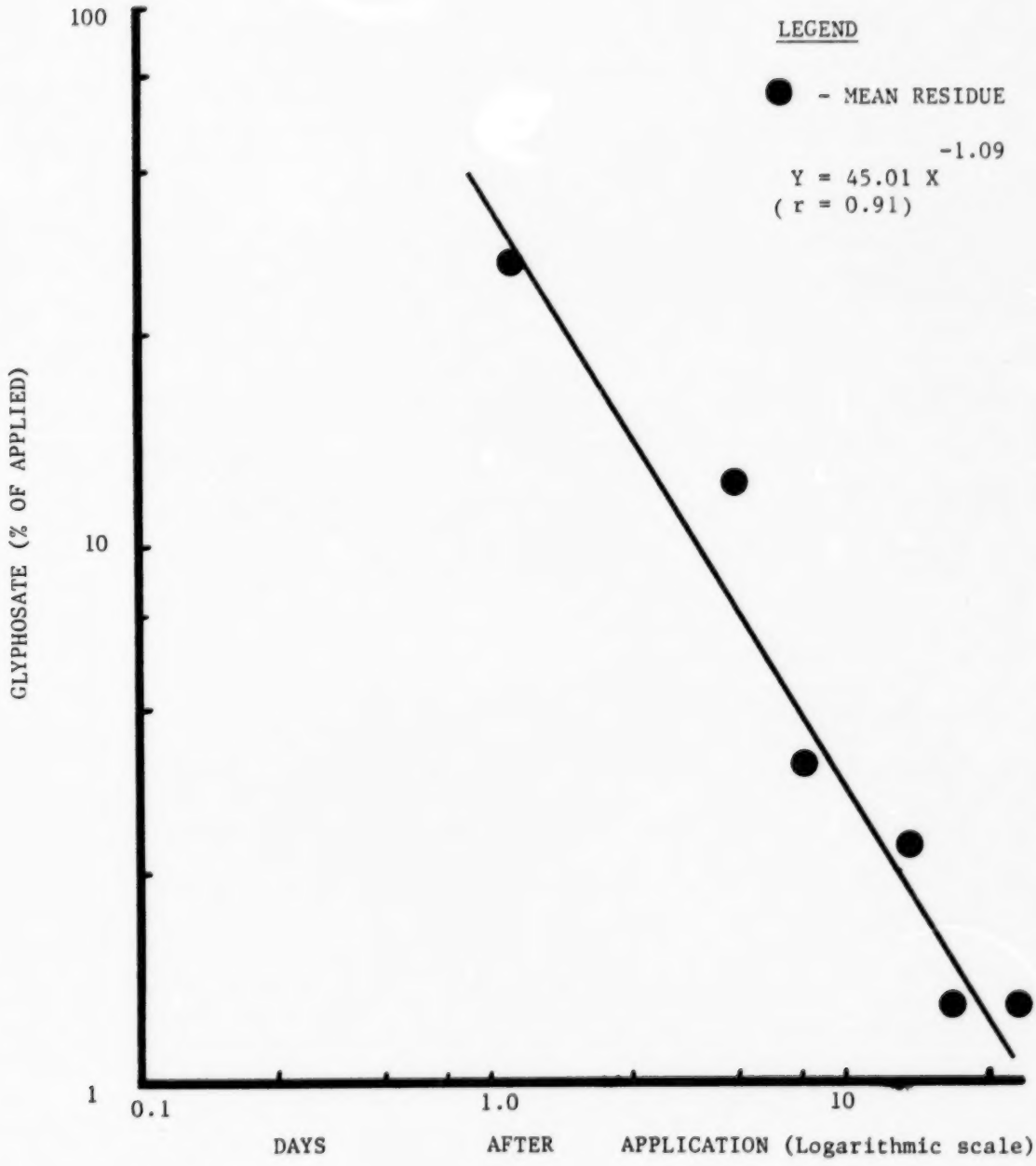

Figure 5: Glyphosate residues (% of applied) in artificial pools containing water and sediments

was necessary to evaluate the persistence of AMPA under local conditions. AMPA residues (Table 4) were calculated as a percent of the estimated potential maximum glyphosate concentrations (Table 7) for each of pools G, H and I (Table 9). The maximum AMPA residue encountered, 2.17% of the estimated potential maximum glyphosate applied, was observed 30 hours after application of Roundup(R) (Table 9). Persistence could be expressed by C_X = 1.66-(0.49 ln x), (r - 0.82), where C_X = concentration of AMPA (% of glyphosate applied) at time X (days). This expression predicted that AMPA residues would decline to 1% of glyphosate applied approximately 3.9 days after application and to 0.01% approximately 30 days after application (Figure 6). Thus it was concluded that AMPA residues rapidly dissipate and would not persist in surface waters of northern Manitoba.

4.2.3 Natural Pond

The uncertainties of volume estimation and extent of mixing associated with natural ponds preclude their use for definitive quantification of dissipation rates. However, they do provide a crude comparison to artificial pools and gross differences in results might signal inadequacies in experimental design.

The persistence of glyphosate in the natural pond (sites A, B and C) was crudely estimated directly from observed values (Table 4). The persistence rate could be expressed by $C_X = 5.13\ X^{-0.55}$, (r = 0.96), where C_X = concentration (µg/L) of glyphosate at time "X" (days). This expression predicted that 50% of the glyphosate

Table 9: AMPA RESIDUES (% OF GLYPHOSATE APPLIED*) IN ARTIFICIAL POOLS CONTAINING WATER AND SEDIMENTS.

Sampling Interval	AMPA (% of Glyphosate Applied)			
	Pool G	Pool H	Pool I	Mean
30 hours	2.17	1.49	0.88	1.51
5 days	1.50	1.56	0.45	1.17
8 days	0.40	0.70	0.24	0.45
15 days	0.13	0.29	0.18	0.20
20 days	0.20	0.11	0.17	0.16
30 days	0.16	0.19	0.11	0.15

* Based upon observed AMPA concentrations (Table 4) and estimated potential maximum concentrations in pools G, H and I (Table 7).

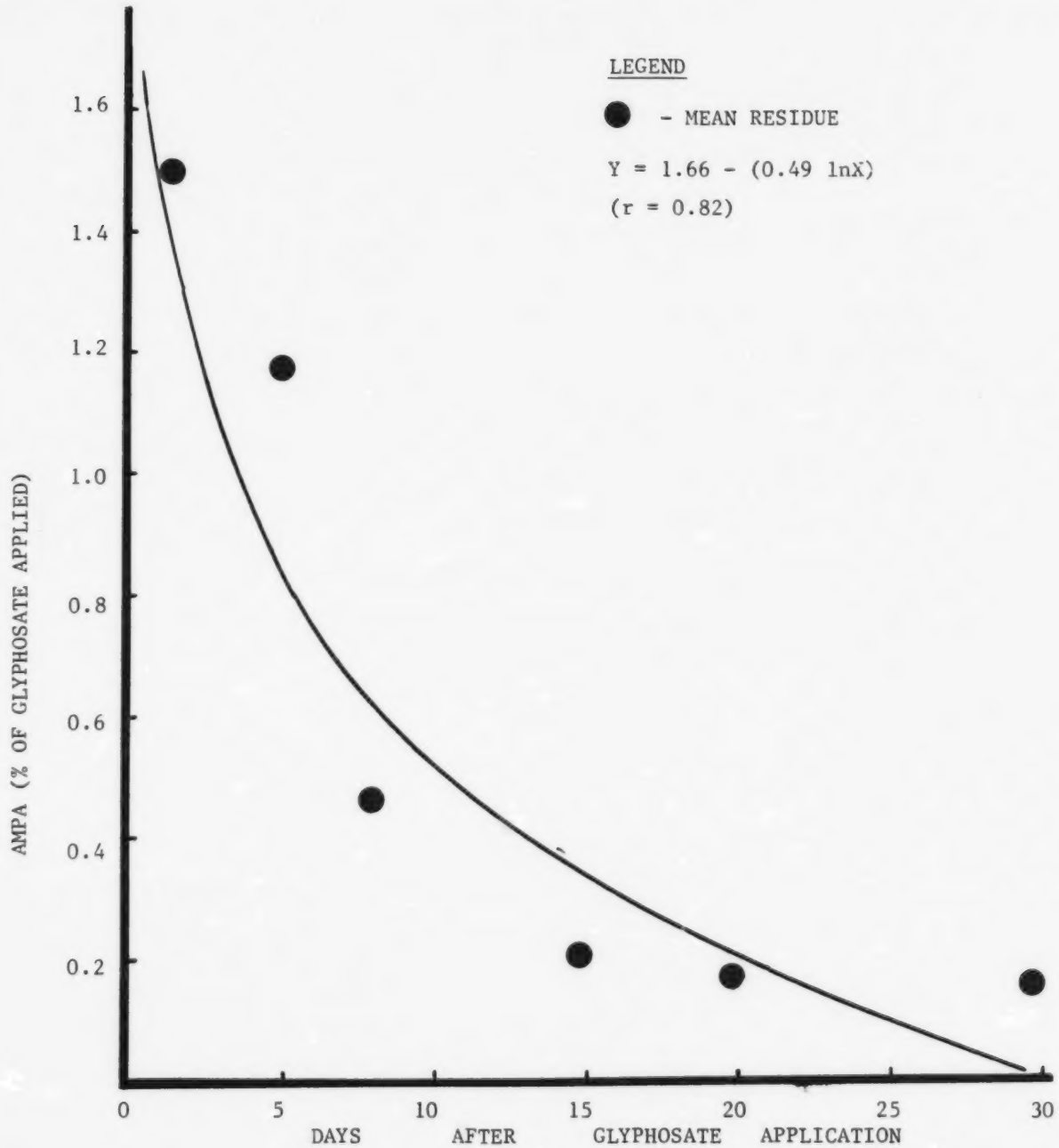

Figure 6: AMPA residues (% of applied) in artificial pools containing water and sediments.

initially applied would be present approximately 1.3 hours after application. Though this was approximately one order of magnitude faster than that predicted from artificial pool data, it confirmed that glyphosate dissipates from water very rapidly under local conditions and that estimates derived from the artificial pools were realistic.

The maximum AMPA residue encountered was 1.4% of total glyphosate measured within 30 minutes after application (Table 4). The absence of AMPA detections beyond the 30-minute sampling interval precluded evaluation of dissipation from the natural pond (Table 4).

4.3 Residues in Sediments

Glyphosate residues (mg/Kg) detected in sediments of both the natural pond and the artificial pools are presented in Table 10. Mean residues ranged from 0.02 $\pm$ 0.02 mg/Kg in natural pond sediments to 0.03 $\pm$ 0.06 mg/Kg in sediments from the artificial pools. The means were not significantly different at $t_{\alpha} = 0.05$. This indicated that sediment adsorptive mechanism(s) operative in the natural pond were not dissimilar to that of the artificial pools. The maximum glyphosate residue encountered in the artificial pools was 0.07 mg/Kg (Table 10). This was approximately 9% of the estimated potential maximum concentration of glyphosate applied (Table 7). The maximum residue encountered in the natural pond was 0.27 mg/Kg at the 30-day sampling interval (Table 10).

The experiment duration was insufficient to address the issue of glyphosate persistence in pond sediments. The data (Table 10)

Table 10: GLYPHOSATE RESIDUES (mg/Kg (DRY WEIGHT))* IN SEDIMENTS

Post-application Sampling Interval	NATURAL PONDS		
	Site A	Site B	Site C
Before spray	<0.01	<0.01	<0.01
30 minutes	<0.01	<0.01	<0.01
30 hours	0.01	0.02	0.09
5 days	<0.01	<0.01	<0.01
8 days	0.01	<0.01	0.01
15 days	0.06	<0.01	<0.01
20 days	<0.01	0.02	<0.01
30 days	0.02	0.02	0.27

Post-application Sampling Interval	ARTIFICIAL POOLS		
	Pool G	Pool H	Pool I
Before spray	<0.01	<0.01	<0.01
30 minutes	<0.01	0.02	<0.01
30 hours	0.03	<0.01	<0.01
5 days	0.02	0.02	<0.01
8 days	0.03	<0.01	0.03
15 days	0.03	0.07	0.03
20 days	0.02	0.06	0.03
30 days	<0.01	0.06	<0.01

* Residues as reported by analytical facility

provided no indication of lessening concentrations at the 30 day sampling interval. Thus the data was supportive of the comparatively lengthy retention (i.e. as compared to residence time in water) by soils and sediments that have been reported in the literature (Comes et al., 1976; Hance, 1976; Hurle and Walker, 1980). Apparently the lengthy retention by soil and sediments poses little subsequent risk since glyphosate inactivated in this manner is considered immobile (Rueppel et al., 1977) and shows little evidence of remobilization (Comes et al., 1976; Edwards et al., 1980).

5.0 CONCLUSIONS

It was concluded that:

1. Glyphosate dissipates rapidly from waters when it enters ponds in northern Manitoba. Presistence in waters may be expressed by $C_X = 45.01\ X^{-1.09}$, where "C_X" is glyphosate concentration at time "X" (days) expressed as a % of glyphosate applied. This expression predicts that 50% of the glyphosate applied would be present approximately 22 hours after application, 10% would be present approximately 4 days after application and that approximately 1% would be present 30 days after application.
2. The presence of sediments is essential for the rapid removal of glyphosate from pond waters in northern Manitoba.
3. AMPA residues dissipate rapidly from waters when glyphosate enters ponds in northern Manitoba. Persistence in surface waters may be expressed by $C_X = 1.66-(0.49\ \ln X)$, where "C_X" is AMPA concentration at time "X" (days) expressed as a % of glyphosate applied. This expression predicts dissipation to 1% of applied glyphosate within approximately 3.9 days of application.
4. Glyphosate residues are relatively persistent in sediments when the herbicide enters ponds in northern Manitoba. This poses little overall environmental risk since the material is considered immobile.

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